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Investigation of the Kinetics of Crystallization of Molten Binary and Ternary Oxide Systems

Quarterly Status Report No. 8

Contract NASW-1301

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SUMMARY

Thirty-one new glass batches were devised in this period increasing the total number of experimental glass varieties studied to 181. These new compositions may be placed into three groups, a four component system in which the mol ratio of magnesia to alumina has been increased to 6 and which includes silica and a rare earth, older glasses which could not previously be successfully fiberized because of too great surface tension where an attempt was made to adjust their surface tension by vanadia additions, and older glasses previously melted with high purity rare earth chemicals which in this quarter were prepared with inexpensive low purity rare earth conglomerates substituted.

From the 181 glass compositions studied to date forty-four varieties of glass fibers have been successfully prepared and many additional test data for these glass fibers are included in this report. These data continue to verify the conclusion that several of the UARL glasses have values for the ratio of Young's modulus to density comparable to any glass now available commercially even though the UARL glasses are made from non-toxic materials. The data also indicate that after storage for a month in a typical laboratory atmosphere, the UARL glass fibers retain higher strength values than do glasses prepared from competitive patent prescriptions.

INTRODUCTION

This report is the eighth quarterly status report for Contract NASW-1301 entitled "Investigation of the Kinetics of Crystallization of Molten Binary and Ternary Oxide Systems". This eighth quarter of the contract started June 1, 1967 and ended August 31, 1967 and forms the first quarter of the second extension to the contract. The primary objective of this program is to gain a better understanding of the essentials of glass formation by measuring the rate at which crystallization occurs and the effect of anti-nucleating agents on the observed crystallization rate for systems which tend to form complex three dimensional structures. Determination of the crystallization rate is carried out by continuously measuring the viscosity and electrical conductivity

of the molten system as a function of time and temperature with checks of surface tension at selected temperatures. Glass formation is greatly increased by employing cooling rates high enough to defeat the formation of the complex many-atom three-dimensional molecule. This view of glass formation justifies the consideration of oxide systems previously thought impractical and allows the search for systems which may yield high strength, high modulus glass fibers to be carried out on an unusually broad basis.

SELECTION AND PREPARATION OF NEW GLASS SYSTEMS FOR EVALUATION

The thirty-one new glass compositions devised, mixed and melted in this three month period included three distinct groups of glass batches as well as some miscellaneous compositions. Eight of the batches were four component systems, i.e. silica, rare-earth, alumina, and magnesia like many of the compositions previously studied but having an unusually high magnesia to alumina molar ratio of six to one or higher. This unusual ratio was selected on the basis of the UARL glass having the highest modulus to density ratio when evaluated by sonic test methods. Four additional glasses of this type were formulated using an inexpensive rare-earth oxalate of low purity (cf. table below) in place of the more expensive high purity (99.9%) cerous oxalate previously employed in several of our experimental glass compositions. Comparative prices are $1.95 per pound in place of $4.12 a pound.

Table I

Approximate Composition of the Rare Earth Oxide Substitute

		wt %			wt %
La_2O_3	Lanthanum oxide	24	Sm_2O_3	Samarium oxide	3
CeO_2	Cerium oxide	48	Gd_2O_3	Gadolinium oxide	2
Pr_6O_{11}	Praseodymium oxide	5	Y_2O_3	Yttrium oxide	0.2
Nd_2O_3	Neodymium oxide	17		Other rare earth oxides	0.8

Since lanthanum oxalate, samarium oxalate, and yttrium oxalate have also been used successfully in compounding our earlier experimental glasses, the chief element of uncertainty in employing this inexpensive substitute is the presence of the praseodymium and neodymium oxides.

The third group of glasses included sixteen older glass compositions to which vanadium pentoxide in amounts from three to nine mol percent was added in an effort to decrease the surface tension of these formulations sufficiently to allow the successful mechanical drawing of fibers with the simple equipment used at UARL and described in our last quarterly report.

All thirty-one experimental glasses were prepared in the usual 500 gram batches using high purity (99.9%) alumina crucibles in air in the UARL Super-Kanthal hairpin element kilns. As usual the ingredients for these batches were completely mixed dry by tumbling and pelletized to facilitate handling. No fining agents were added to the batches since the use of at least one constituent as either the oxalate or carbonate has proven sufficient in general to yield water-white optical glass free of seed and bubbles when the mix is held at a temperature of 1540°C or higher for a period of two hours. The highly tinctorial materials used in this period eliminated any optical examination of the glass obtained but it is presumed that they aid, not interfere, with the fining action customarily obtained.

CHARACTERIZATION OF GLASS FIBERS PRODUCED FROM EXPERIMENTAL GLASS COMPOSITIONS

Results on many of the experimental glass fibers sent to Lowell Institute of Technology for evaluation became available in this period. These results are completely summarized in Table II and are compared to values for the elastic moduli of the same glasses as determined by sonic testing. The specimens measured at Lowell Institute of Technology were tested for modulus using an Instron CRE tester operated with a machine speed of 0.2 inches per minute, a chart speed of 20 inches per minute, a gage length of 5 inches, and a full scale capacity of 1.0 pounds. Air actuated clamps were used with flat rubber coated faces.

Twenty specimens were taken from approximately the center portion of each spool. The specimens were eight inches long, with about one yard of fiber being discarded between each specimen. It was not always possible to select fibers in exactly this manner because many of the spools had discontinuous odd lengths of fiber, but in general, the specimens selected represent the middle 20 yards of fiber received for testing.

Three fiber diameter measurements were made in the middle three-inch portion of each eight-inch specimen. Measurements were made using a monocular microscope equipped with an eye piece reticule and operated with a magnification of 774 (18 x eye piece, 43 x objective). Each reticule division was equal to 0.092 mils.

The average of the twenty determinations for each fiber is shown in Table II together with the maximum and minimum value of modulus. Statistical examination of the data for samples 83 and 126 is shown in Table III.

Table II

Recapitulation of All Data for Elastic Moduli of Glasses Successfully Made Into Fibers

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Glass Number	Composition in Mol Percent																Dynamic Moduli Values								Static Moduli Values				
	SiO_2	Al_2O_3	MgO	CaO	Y_2O_3	La_2O_3	Ce_2O_3	Sm_2O_3	Ta_2O_5	ZrO_2	SrO	Na_2O	Li_2O	B_2O_3	ZnO	TiO_2	Glass Number	Density gm/cm³	Velocity C (cm/sec) x 10^5 (Bar)	Velocity C (cm/sec x 10^5) UARL-1	Velocity C (cm/sec x 10^5) UARL-2	Velocity C (cm/sec x 10^5) Morgan	Velocity C (cm/sec x 10^5) Most Probable	σ^2 - cm²/sec² x 10^{10}	$\rho\sigma^2$ = E(kg x 10^5/cm²)	E(dynamic) psi x 10^6	E(static) min psi x 10^6	Lowell E(static) max psi x 10^6	E(static) aver psi x 10^6 20 tests	UARL Static E psi x 10^6	WPAFB Static E psi x 10^6	(10 tests) psi x 10^6 UARL(static) Bulk E
14	52.3	18.7	29.2														14													15.07
25	49.5	20.4	11.1								17.8						25	2.9672								9.5	16.3	12.3			
40	58.4	20.9	16.3				4.53										40	2.9574	5.74	5.12			5.74	32.9	9.72	13.80	9.3	29.2	16.2			
56	67.8												26.8	0.37	4.91		56	2.4368	5.79	6.20		5.78	5.79	33.5	8.16	11.60	8.9	12.4	10.7			
62	54.6	15.2	29.2				1.0										62	2.7036	6.5	6.32		6.29	6.31	39.8	10.75	15.30	13.1	15.4	14.0	14.7		
63	54.6	15.6	28.9														63	2.6847	6.3	6.65	6.18	6.53	6.43	41.3	11.10	15.78	9.0	16.7	13.0	14.4	13.7	14.71
64	54.6	15.5	28.8		1.39	0.95											64	2.6818	6.26	5.95		6.03	5.99	35.9	9.63	13.67	10.9	24.3(18.9)	14.7			14.78
65	54.6	15.6	28.9					0.89									65	2.7197	6.24	6.51			6.375	40.7	11.07	15.75	12.3	15.2	13.8				15.57
66	53.7	15.3	28.3							2.56							66	2.6784		6.63			6.63	43.9	11.69	16.63							15.20
67	54.7	15.3	29.3						0.76								67	2.6535	6.58	6.58			6.58	43.3	11.47	16.33	10.0	15.9	12.7				15.14
68	53.4	18.3	28.8														68	2.6295	6.58	6.52		6.54	6.55	42.9	11.27	16.05	11.8	17.1(14.9)	13.7			15.36
69	57.3	14.6	28.3														69	2.5910	6.39	6.52			6.455	41.7	10.4	14.80	11.9	15.3	13.6			
70	55.3	12.6	29.3		2.83												70	2.7526	6.58	6.41	6.33	6.44	6.44	41.5	11.42	16.25	10.2	18.4	13.5	14.9	13.6	15.23
70																	70										11.0	16.6	13.3			
71	49.4	14.1	36.5														71	2.6627		6.85			6.85	46.9	12.48	17.75	9.5	16.6	13.7			
72	56.9	15.1	25.4				2.60										72	2.8877	6.06	6.09	6.25		6.08	37.0	10.69	15.20	8.4	17.7(15.4)	12.5			(15.14)15.15
73	59.1	8.66	26.4		3.13		2.70										73	3.0152	6.125			6.05	6.09	37.1	11.02	15.70	12.8	19.7	15.1	13.5		15.14
74	56.1	9.6	30.3		4.3												74	2.9983		5.92			5.92	35.0	10.5	14.95	11.4	19.5(17.2)	13.8			
75	61.2			21.2								17.6					75	2.6340		5.69			5.69	32.4	8.53	12.12	5.0	19.3(14.1)	9.8			
76	61.9			26.2								11.9					76			5.64			5.64	31.8			8.2	14.8	10.4			11.51
77	61.2			31.8								7.0					77			5.53	5.78		5.66	32.0			9.0	13.1	11.0			12.16
82	54.3	24.5	18.1							1.6		0.05					82	2.5875	6.49	6.65	6.57		6.61	43.7	11.30	16.08	11.2	15.9	13.3			
83	42.9		11.3	11.8			0.86			0.81	22.2		5.06			5.06	83	2.8876	6.527	6.4975			6.512	42.4	12.03	17.11	11.9	20.9	15.05			
102	45.0	11.0	11.0	11.0									11.0		11.0		102	2.9188		4.82			4.82	23.25	6.79	9.66	8.0	21.6(17.1)	13.3			
108	65.0		7.0	7.0	7.0								7.0		7.0		108										6.8	17.2	12.5			
110	55.56	22.22	22.22														110	2.6128									9.9	18.5	13.8			
114	51.7	22.5	15.8		10.0												114	3.2237	6.11	6.396	5.93	6.68	6.28	39.4	12.72	18.10	8.3(12.3)	19.0	15.1	17.4	14 to 17	16.5
126	49.67	22.5	13.83		14.0												126	3.4634	6.00				6.00	36.0	12.44	17.72	11.4	19.7	16.15			
127	60.0	10.0	20.0		10.0												127	3.2553	6.06	6.09			6.075	36.9	12.62	17.12	12.7	19.4	15.2			
129	50.0	13.33	26.67		10.0												129	3.3105	6.03	6.36			6.195	38.4	12.70	18.08	12.4	21.8	16.5			
131	70.0	6.66		13.3	10.0												131	3.1200	5.89	5.86			5.87	34.4	10.73	15.28	10.0	16.6	12.5			
135	54.3	15.6	28.9			1.8											135	2.6303	6.16				6.16	37.9	9.98	14.19	11.4	16.7	13.3			
136	53.3	15.6	28.9			2.0											136	2.8035	6.06				6.08	37.0	10.37	14.75	10.9	17.9(15.9)	13.5			
137	51.3	15.6	28.9			4.0											137	3.0834	6.08				6.08	37.0	11.4	16.22	11.1	17.6	13.9			
138	47.3	15.6	28.9			8.0											138	3.5498	5.66				5.66	32.0	11.36	16.15	6.3	16.0	12.2			16.53
140	47.3	15.6	27.9			8.0	1.0										140			5.64			5.64	31.8			13.4	17.2	15.0			
155	49.4	7.05	36.5						7.05								155	3.2541									9.6	17.3	14.7			
159	57.4	6.6	28.0		8.0												159										5.3	27.4	15.0			

82 - Houze Glass - U.S. 3,044,888
83 - Owens-Corning - U.S. 3,122,277 (BeO)

Table III

Statistical Results

	Sample 83	Sample 126
Mean $\bar{x}$ (1st twenty samples)	15.8	16.4
Standard deviation, S	1.95	1.82
Standard error, $S_{\bar{x}}$	0.44	0.41
Limits for expected mean at		
99% probability	14.5-17.1	15.2-17.6
95% probability	14.9-16.7	15.5-17.3
Mean $\bar{x}$ (twenty additional runs)	14.3	15.9

As may be seen in Table II the sonic and stress-strain methods of measuring elastic moduli fail to yield concordant results. This is true not only for this laboratory but also in general for all other laboratories who have used both methods and is believed to be due to the fact that the sonic method more nearly measures an instantaneous value of the modulus than does the stress-strain machine type of testing. Many applications envisioned for the UARL glass fiber are dependent on the long-term properties of the fiber which may be more closely correlated with the mechanical test and this method is therefore selected as preferable for modulus evaluation. Both sets of data show that several of the UARL glass compositions yield values for Young's modulus superior to the two chief experimental competitive glasses when all glasses to be tested are prepared, melted, fiberized, and tested in identical procedures at UARL for direct comparative evaluation.

The apparatus for measuring the strength of the UARL glasses when freshly prepared and in an inert atmosphere is not yet operative. But strength evaluations made after the glass fibers have been wound on the spool without lubricant or surface treatment of any sort and stored in a typical laboratory atmosphere for five to six weeks show that several of the UARL glasses retain higher strength values than do the two competitive glasses tested under identical conditions. Table IV shows the average result of twenty breaking strength determinations for several glasses.

Table IV

Breaking Strength After Five to Six Weeks Storage
in a Typical Laboratory Atmosphere

Sample	Breaking Strength	
	Pound	Pounds/Square Inch x 10^4
62-3	0.157	13.4
72-4	0.062	13.0
73	0.215	16.5
82-2*	0.189	13.4
83**	0.253	9.8
126	0.327	22.2
127	0.375	14.9
129-2	0.164	16.7

* Sample prepared from teachings of U.S. Patent 3,044,888 Houze Glass

** Sample prepared from teachings of U.S. Patent 3,122,277 (BeO) Owens-Corning

All samples prepared, melted, fiberized and tested in identical procedures.